

**PATENT APPLICATION**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:

ARCELLA et al

Group Art Unit: Not yet assigned

Serial No.: New Application

Examiner: Not yet assigned

Filed: February 25, 2002

Attorney Dkt. No.: 108910-00054

For: POROUS HYDROPHILIC MEMBRANES

**PRELIMINARY AMENDMENT**

Commissioner for Patents  
Washington, D.C. 20231

February 25, 2002

Sir:

Prior to calculation of the filing fees and initial examination of the application, please amend the above-identified application as follows:

**IN THE CLAIMS:**

Please amend claims 3-6, 9-15, 17, 19-20, and 22-24 as follows. A copy of the marked up original claims is attached to this response showing the changes as set forth in amended 37 CFR 1.121.

3. (Amended) Membranes having pores totally occluded to gases according to claim 1, containing an ionomer amount higher than about 30% by weight.

4. (Amended) Membranes having pores partially occluded to gases according to claim 1, containing an ionomer amount lower than about 20% by weight.

5. (Amended) Membranes according to claim 1, wherein the porous support is formed by (per)fluoropolymers, preferably PTFE, still more preferably bistretched PTFE.

6. (Amended) Membranes according to claim 1, wherein the ionomers are (per)fluorinated polymers and they preferably have SO<sub>3</sub>H and/or -COOH, preferably SO<sub>3</sub>H, functionality, and an equivalent weight such as to result amorphous.

9. (Amended) Membranes according to claim 7, wherein the fluorinated monomers of type (B) are selected from the following:

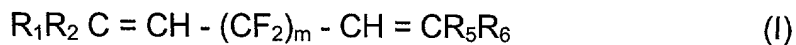
- F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F;
- F<sub>2</sub>C=CF-O-[CF<sub>2</sub>-CXF-O]<sub>n</sub>-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F

wherein X = Cl, F or CF<sub>3</sub>; n = 1-10;

- F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F
- F<sub>2</sub>C=CF-Ar-SO<sub>2</sub>F wherein Ar is an aryl ring;
- F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-COF
- F<sub>2</sub>C=CF-O-[CF<sub>2</sub>-CXF-O]<sub>n</sub>-CF<sub>2</sub>-CFX-COF

wherein X = Cl, F or CF<sub>3</sub>; n = 1-10.

10. (Amended) Membranes according to claim 1, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:



wherein:

m = 2-10, preferably 4-8;

R<sub>1</sub>, R<sub>2</sub>, R<sub>5</sub>, R<sub>6</sub>, equal to or different from each other, are H or C<sub>1</sub>-C<sub>5</sub> alkyl groups.

11. (Amended) Membranes according to claim 1, wherein the ionomers comprise:

- monomeric units deriving from TFE;
- monomeric units deriving from CF<sub>2</sub>=CF-O-CF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

12. (Amended) Membranes according to claim 1, wherein the amorphous ionomer shows a substantial absence of crystallinity.

13. (Amended) Membranes according to claim 1, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.

14. (Amended) Membranes according to claim 1, wherein the (per)fluorinated ionomers are crosslinked.

15. (Amended) Membranes according to claim 1, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.

17. (Amended) Use of the membranes according to claim 1 in electrochemical cells.

19. (Amended) Use of the membranes according to claim 4, wherein the fuel cells are used and an air pressure is used at the cathode side higher than that of the hydrogen at the anode side, the fed hydrogen coming from reforming and therefore containing CO.

20. (Amended) A process for preparing hydrophilic porous membranes according to claim 1, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing hydrophilic groups, preferably having a  $-SO_3H$  or  $-COOH$  functionality, said process comprising the following steps:

- a) impregnation of the porous support formed by the (per)fluorinated polymer, with a (per)fluorinated ionomer having hydrolysable functions, preferably  $-SO_2F$ ,  $-COOR$ ,  $-COF$ , wherein R is a  $C_1$ - $C_{20}$  alkyl radical or a  $C_6$ - $C_{20}$  aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight until obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures between the room temperature and  $120^\circ C$ , preferably between  $15^\circ C$  and  $40^\circ C$ ; the so impregnated membrane is subjected to thermal treatment at temperatures from  $50^\circ$  to  $200^\circ C$ , preferably from  $120^\circ$  to  $160^\circ C$  until substantial removal of the solvent and

obtainment of a substantially transparent membrane, optionally step a) is repeated until the membrane appears substantially transparent;

- b) treatment of the membrane obtained in a) with inorganic strong, preferably aqueous, alkalis, i.e. bases which are completely dissociated in water, to obtain the conversion of the functional groups into hydrophilic groups, preferably from  $-\text{SO}_2\text{F}$  into  $-\text{SO}_3^-$ , and of the  $-\text{COOR}$ ,  $-\text{COF}$  groups into  $-\text{COO}^-$  groups;
- c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;
- d) optionally treatment with water at temperatures in the range  $50^\circ\text{C}$  -  $100^\circ\text{C}$ , in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.

22. (Amended) A process according to claim 20, wherein in step b) the used strong alkalis are the hydroxides of the Group Ia metals.

23. (Amended) A process according to claim 20, wherein at the end of step b) washings with water are carried out until a neutral pH of the washing waters is obtained.

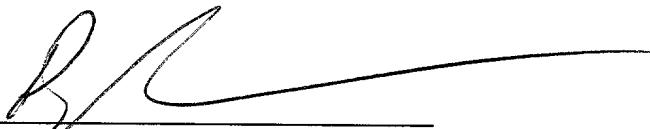
24. (Amended) A process according to claim 20, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.

### **REMARKS**

Claims 1-25 are pending in this application. By this Amendment, claims 9-15, 17, 19-20, and 22-24 are amended to correct the multiple dependency thereof and to place this application into better condition for examination. No new matter has been added.

In the event that there are any fees due with respect to the filing of this paper, please charge Deposit Account No. 01-2300.

Respectfully submitted,

  
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Douglas H. Goldhush  
Registration No. 33,125

**Customer No. 004372**

ARENT FOX KINTNER PLOTKIN & KAHN, PLLC  
1050 Connecticut Avenue, N.W.,  
Suite 400  
Washington, D.C. 20036-5339  
Tel: (202) 857-6000  
Fax: (202) 638-4810

DHG:scc

Enclosures: Marked-up Copy of Amended Claims

**MARKED-UP COPY OF AMENDED CLAIMS**  
**ATTY. DOCKET NO. 108910-00054**

3. (Amended) Membranes having pores totally occluded to gases according to [claims 1-2] claim 1, containing an ionomer amount higher than about 30% by weight.

4. (Amended) Membranes having pores partially occluded to gases according to [claims 1-2] claim 1, containing an ionomer amount lower than about 20% by weight.

5. (Amended) Membranes according to [claims 1-4] claim 1, wherein the porous support is formed by (per)fluoropolymers, preferably PTFE, still more preferably bistretched PTFE.

6. (Amended) Membranes according to [claims 1-5] claim 1, wherein the ionomers are (per)fluorinated polymers and they preferably have SO<sub>3</sub>H and/or -COOH, preferably SO<sub>3</sub>H, functionality, and an [equivalent] equivalent weight such as to result amorphous.

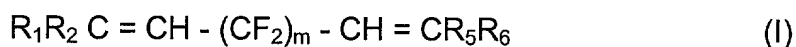
9. (Amended) Membranes according to [claims 7-8] claim 7, wherein the fluorinated monomers of type (B) are selected from the following:

- F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F;
  - F<sub>2</sub>C=CF-O-[CF<sub>2</sub>-CXF-O]<sub>n</sub>-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F
- wherein X = Cl, F or CF<sub>3</sub>; n = 1-10;
- F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F

- $\text{F}_2\text{C}=\text{CF}-\text{Ar}-\text{SO}_2\text{F}$  wherein Ar is an aryl ring;
- $\text{F}_2\text{C}=\text{CF}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{COF}$
- $\text{F}_2\text{C}=\text{CF}-\text{O}-[\text{CF}_2-\text{CXF}-\text{O}]_n-\text{CF}_2-\text{CFX}-\text{COF}$

wherein X = Cl, F or  $\text{CF}_3$ ; n = 1-10.

10. (Amended) Membranes according to [claims 1-9] claim 1, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:



wherein:

m = 2-10, preferably 4-8;

$\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_5$ ,  $\text{R}_6$ , equal to or different from each other, are H or  $\text{C}_1$ - $\text{C}_5$  alkyl groups.

11. (Amended) Membranes according to [claims 1-10] claim 1, wherein the ionomers comprise:

- monomeric units deriving from TFE;
- monomeric units deriving from  $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ ;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

12. (Amended) Membranes according to [claims 1-11] claim 1, wherein the amorphous ionomer shows a substantial absence of crystallinity.



13. (Amended) Membranes according to [claims 1-11] claim 1, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.

14. (Amended) Membranes according to [claims 1-13] claim 1, wherein the (per)fluorinated ionomers are crosslinked.

15. (Amended) Membranes according to [claims 1-13] claim 1, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.

17. (Amended) Use of the membranes according to [claims 1-16] claim 1 in electrochemical cells.

19. (Amended) Use of the membranes according to claim [18] 4, wherein [in] the fuel cells [the membranes of claim 4] are used and an air pressure is used at the cathode side higher than that of the hydrogen at the anode side, the fed hydrogen coming from reforming and therefore containing CO.

20. (Amended) A process for preparing hydrophilic porous membranes according to [claims 1-16] claim 1, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing

hydrophilic groups, preferably having a  $-\text{SO}_3\text{H}$  or  $-\text{COOH}$  functionality, said process comprising the following steps:

- a) impregnation of the porous support formed by the (per)fluorinated polymer, with a (per)fluorinated ionomer having hydrolysable functions, preferably  $-\text{SO}_2\text{F}$ ,  $-\text{COOR}$ ,  $-\text{COF}$ , wherein R is a  $\text{C}_1\text{-C}_{20}$  alkyl radical or a  $\text{C}_6\text{-C}_{20}$  aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight until obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures between the room temperature and  $120^\circ\text{C}$ , preferably between  $15^\circ\text{C}$  and  $40^\circ\text{C}$ ; the so impregnated membrane is subjected to thermal treatment at temperatures from  $50^\circ$  to  $200^\circ\text{C}$ , preferably from  $120^\circ$  to  $160^\circ\text{C}$  until substantial removal of the solvent and obtainment of a substantially transparent membrane, optionally step a) is repeated until the membrane appears substantially transparent;
- b) treatment of the membrane obtained in a) with inorganic strong, preferably aqueous, alkalis, i.e. bases which are completely dissociated in water, to obtain the conversion of the functional groups into hydrophilic groups, preferably from  $-\text{SO}_2\text{F}$  into  $-\text{SO}_3^-$ , and of the  $-\text{COOR}$ ,  $-\text{COF}$  groups into  $-\text{COO}^-$  groups;
- c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;

- d) optionally treatment with water at temperatures in the range 50°C - 100°C, in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.

22. (Amended) A process according to [claims 20-21] claim 20, wherein in step b) the used strong alkalis are the hydroxides of the Group Ia metals.

23. (Amended) A process according to [claims 20-22] claim 20, wherein at the end of step b) washings with water are carried out until a neutral pH of the washing waters is obtained.

24. (Amended) A process according to [claims 20-23] claim 20, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.